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SOME EFFECTS OF HEAVY PARTICLE IRRADIATION  
OF AQUEOUS ACETIC ACID

Warren M. Garrison, Herman R. Haymond  
and Boyd M. Weeks

August, 1953

Berkeley, California

SOME EFFECTS OF HEAVY PARTICLE IRRADIATION  
OF AQUEOUS ACETIC ACID\*Warren M. Garrison, Herman R. Haymond  
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University of California,  
Berkeley, California

August, 1953

In the preceding papers of this symposium, consideration has been given to the problem of determining the mechanism of the decomposition of water by high energy radiation. Formation of the chemically reactive radicals H and OH and the decomposition products  $H_2$  and  $H_2O_2$  have been critically investigated in the light of available evidence. According to present concepts<sup>1-5</sup> of the mechanism of the indirect action of radiation on solutes, the preliminary chemical effect is the dissociation, by ionization and excitation, of water molecules to give the H and OH radicals. The observed chemical changes in irradiated solutions are attributed to subsequent reactions of H and OH radicals with one another and with solute molecules. The relative amounts of those radicals that combine to form  $H_2$  and  $H_2O_2$  and of those that are available for reaction with added solute depend upon the ionization density of the effective radiation. Radiation chemical reactions in dilute solution have been discussed in the previous papers in some detail, primarily however, from the standpoint of determining the yields of free H and OH. In studies of this type, in which the principal objective is the determination of the mechanism of water decomposition, the use of relatively simple solute systems is advantageous because the complete mechanism of the overall reaction must be determined. Radiolysis of most aquo-organic systems however, usually results in the formation of a spectrum of reaction products many of which may be formed in amounts which are difficult if not impossible to determine by classical analytical procedures. The development of radio metric and chromatographic techniques during the last few years has made it possible to study quantitatively many of the

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systems which were previously not amenable to investigation. Recently, as part of a general investigation<sup>6-8</sup> of radiation induced reactions of organic substances in aqueous solution, we have applied these techniques to a study of the products formed in aqueous acetic acid by heavy particle irradiation. Some of the methods and results are described in the present paper.

The 60-inch cyclotron at the Crocker Laboratory was used as a radiation source. The acetic acid solutions were irradiated in all-glass target cells of the type shown in Figs. 1, 2 and 3. The window in each cell had an average thickness of approximately 3 mils over the irradiated area. Solutions in cells 1 and 2 were aerated with oxygen or helium during irradiation to control the oxygen concentration and to obtain adequate mixing of products. A glass stirrer could be inserted into cell 2. Evacuated solutions were irradiated in cell 3. Mixing in this case was obtained by rocking the cell about the axis of the beam. The cells were supported in a bracket which was in turn attached to the target shutter assembly shown in Fig. 4. The cyclotron beam entered the front plate (1) and was delimited by the aperture (2). The defined beam then passed through a one mil aluminum foil which was retained in position by (3) and the shutter arrangement (5, 5a). The irradiation period could be accurately controlled by the shutter (5b). The beam monitoring circuit is shown schematically. The energy of the helium ion beam was evaluated from range-energy relationships and from calorimetric data.

In preliminary product identification studies<sup>8</sup>, 10 ml volumes of 0.25 M acetic acid containing from 50 to 100 microcuries of  $\text{CH}_3\text{C}^{14}\text{OOH}$  were irradiated in cell 1 with 35 Mev helium ions at a beam intensity of 0.1 microamperes. The non-volatile fraction, separated by evaporation in vacuo, was chromatographed on a silicic acid column using a procedure based on the method of Marvel and Rands.<sup>9</sup> Fig. 5 shows a typical elution curve for a total dose of  $1.4 \times 10^{20}$  ev/ml. Figs. 6 and 7 are elution curves corresponding to radiation doses of  $5.8 \times 10^{20}$  ev/ml and  $19.9 \times 10^{20}$  ev/ml. Below a dose of  $1 \times 10^{20}$  ev/ml peak I only appeared. The ordinates are plotted in arbitrary units. Fig. 8 shows the results of a similar bombardment in which 80 ml of 0.25 M acetic acid containing 200 microcuries of  $\text{CH}_3\text{C}^{14}\text{OOH}$  was irradiated in cell 2 for a total dose of  $44.6 \times 10^{20}$  ev/ml. In this case both the  $\text{C}^{14}$  activity and the acid titre of the effluent were determined. The correspondence between the two curves indicates that the  $\text{C}^{14}$  activity peaks correspond to labelled acid products. For identification studies,  $\text{C}^{14}$  labelled products

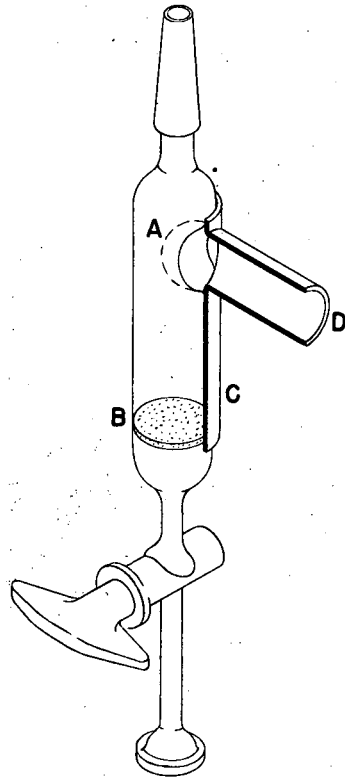


Fig. 1

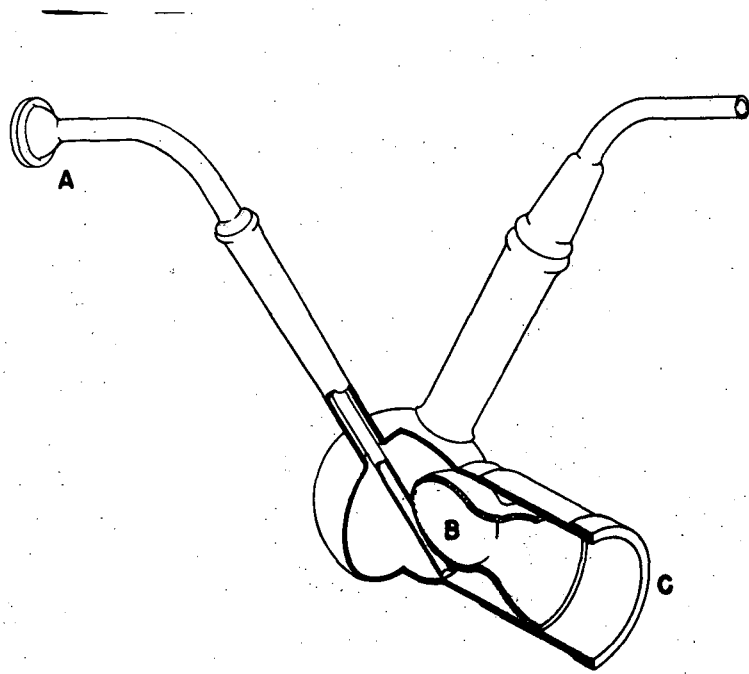


Fig. 2



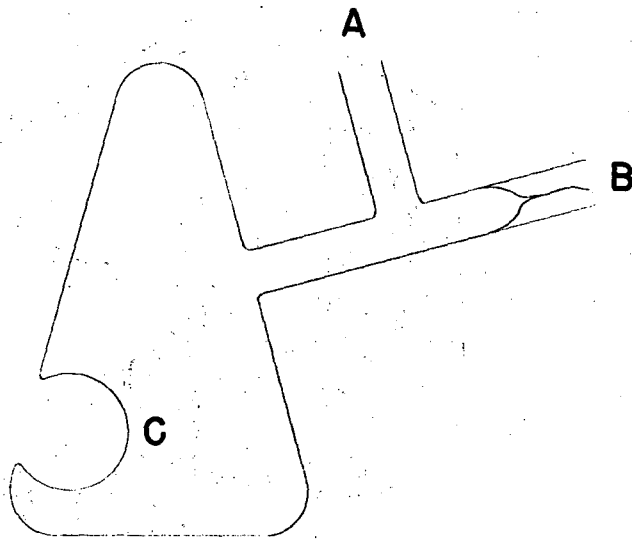


Fig. 3

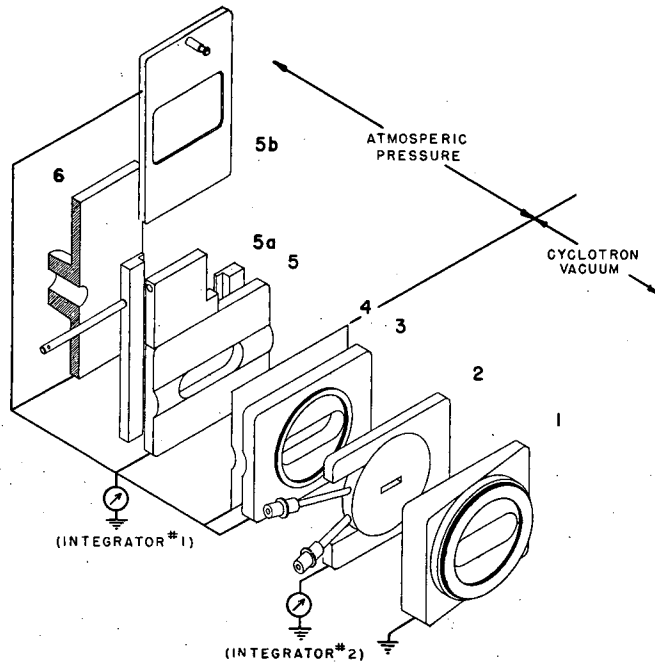


Fig. 4. (Target assembly and beam monitoring circuit. (From W. M. Garrison et al, J. Am. Chem. Soc., 75, 2459 (1953)).

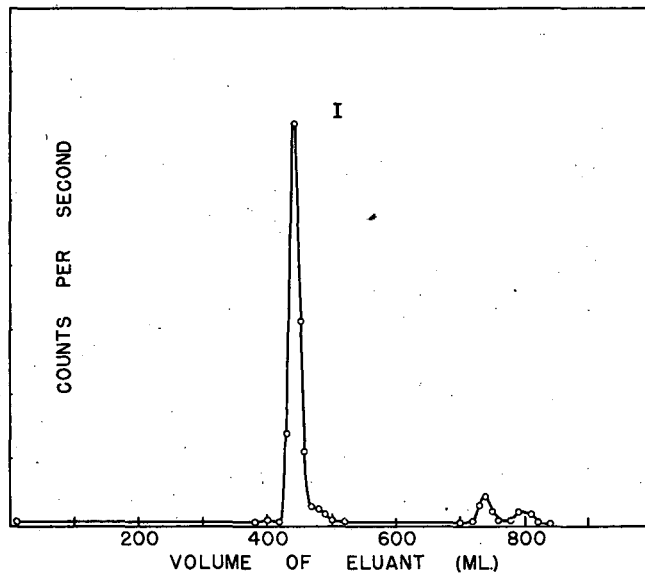


Fig. 5. Radiation dose,  
 $1.4 \times 10^{20}$  ev/ml.

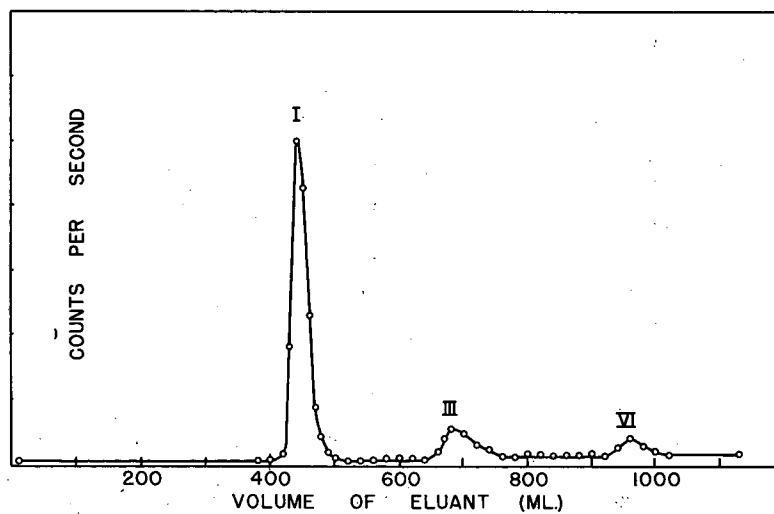


Fig. 6. Radiation dose,  
 $5.8 \times 10^{20}$  ev/ml.

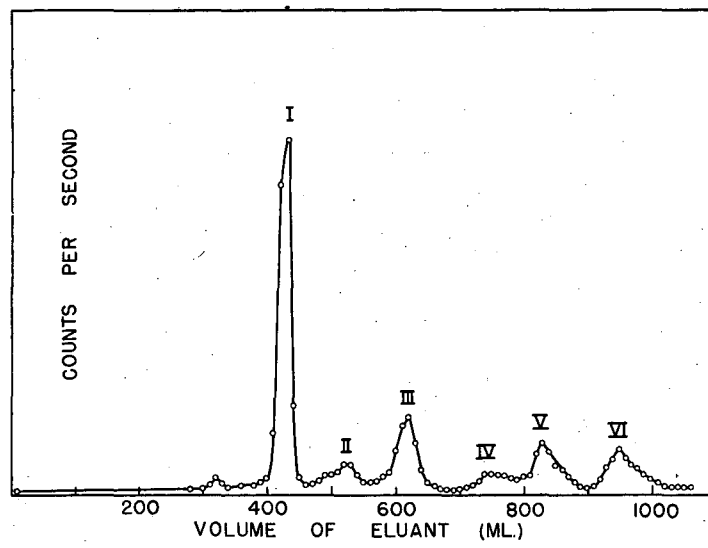


Fig. 7. Radiation dose,  
 $19.9 \times 10^{20}$  ev/ml.

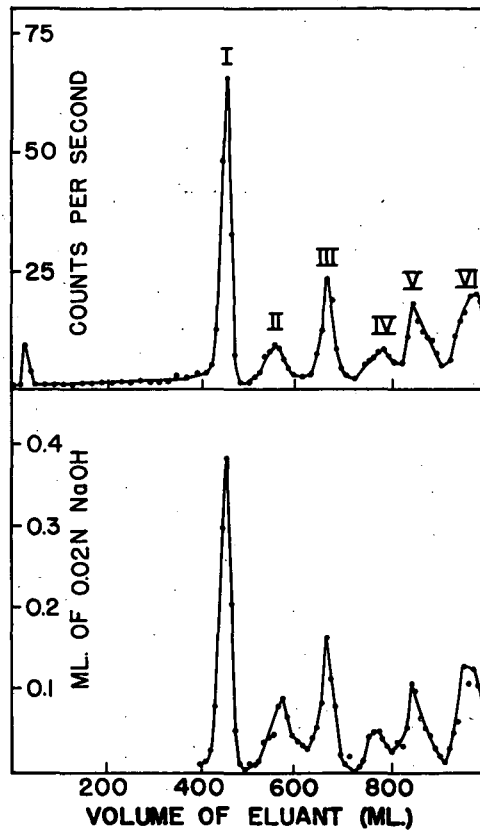
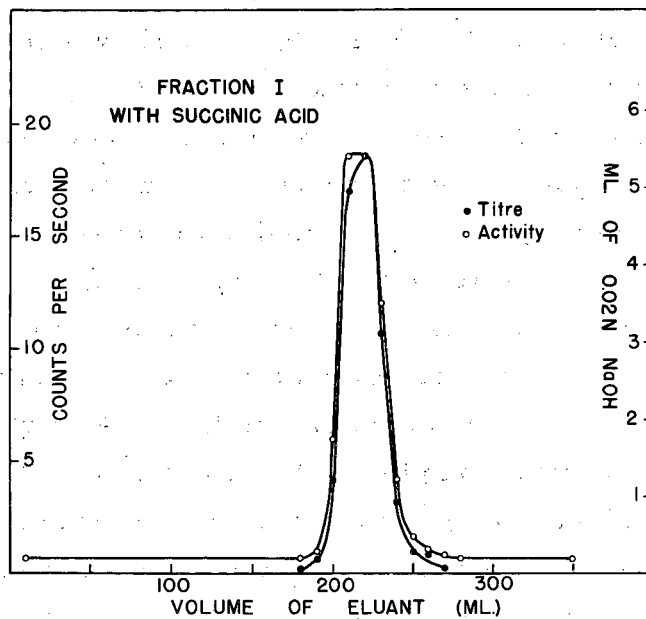


Fig. 8. Comparison of titre and activity, radiation dose,  $44.6 \times 10^{20}$  ev/ml. (From W. M. Garrison, et al, J. Am. Chem. Soc., 75, 2459 (1953)).

of high specific activity were obtained by irradiating in cell 1, 10 ml volumes of 0.25 M acetic acid containing as much as 250 to 300 microcuries of  $\text{CH}_3\text{C}^{14}\text{OOH}$ . In this way it was possible to isolate the product peaks in amounts which gave  $\text{C}^{14}$  counting rates of several hundred counts per second and a titre of less than 0.01 ml of 0.01 N sodium hydroxide. Samples of each of these peaks were then co-chromatographed with added authentic acids in milligram amounts. Identification of the product depended on an exact correspondence between titre and activity in the elution curves from two or more chromatograph methods. These methods have been discussed in detail elsewhere.<sup>8</sup> Figs. 9 and 10 show typical co-elution curves of fraction I with succinic acid and fraction III with tricarballic acid. In all cases these fractions showed only a single acid product species. Peaks II, V and VI, however, were each found to be composed of a mixture of acids. These were fractionated chromatographically. Malonic, malic and citric acids were found to be the principal products in II, V and VI respectively.

Quantitative studies have been made at radiation doses of  $1 \times 10^{21}$  ev/ml and below. In this range, the succinic acid yield is independent of beam intensity and shows a linear dependence on radiation dose. At higher doses the kinetics become considerably more complex with the formation of malonic, malic, citric and other as yet unidentified reaction products. A quantitative determination of succinic acid was made by direct titration of the silicic acid column eluant in the appropriate region. The details of this procedure and methods for determination of hydrogen peroxide, organic peroxides and gaseous products have been discussed.<sup>8</sup>

Table IA shows the effect of acetic acid concentration on the radiation yield of succinic acid and hydrogen peroxide in evacuated solutions irradiated with 35 Mev helium ion at a beam intensity of 0.20 microamperes for a total dose of  $3.8 \times 10^{20}$  ev/ml. Target cell 3 was used in these studies. In the concentration range .0625 M to 1.0 M it is seen that the radiation yields of succinic acid and hydrogen peroxide increase with acetic acid concentration and approach a limiting value. That the observed leveling off in product yield is not the result of a product concentration gradient in the irradiation zone is indicated by the agreement between the results in Table IA and IB. In the latter experiments, a glass stirrer was rotated at 1700 r.p.m. directly behind the irradiation zone. The solutions were air free and were flushed with helium during irradiation.



**Fig. 9. Typical co-elution curve of fraction I with authentic succinic acid.**



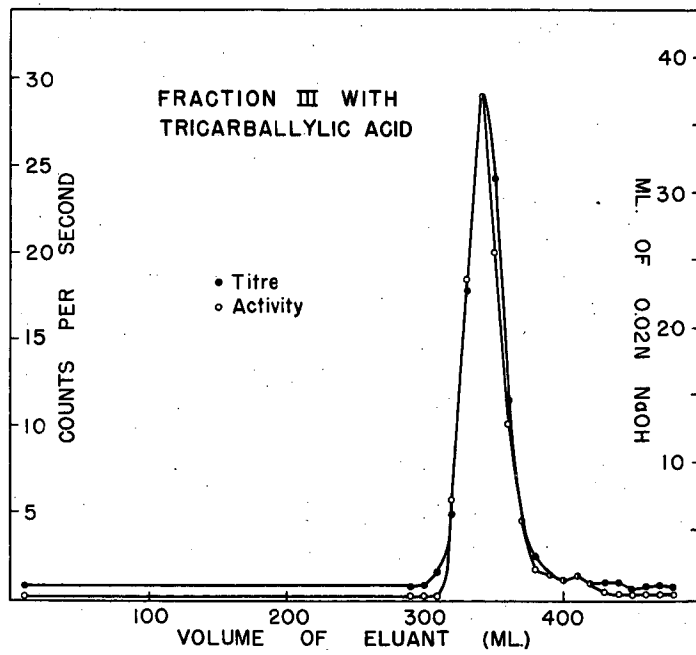


Fig. 10. Typical co-elution curve of fraction III with authentic tricarballic acid.

The decreases in the radiation yield of succinic acid and hydrogen peroxide with acetic acid dilution indicates that reaction with acetic acid is not the only process for radical removal. Nor, apparently, is the falling off in succinic acid yield caused by competing secondary reactions involving succinic acid and tricarballic acid since their radiation products do not appear in appreciable amounts at this dose level. Although it is not possible to present a complete kinetic scheme for the radiolysis of acetic acid solution it is of interest to note that many of the observations can be interpreted if it is assumed that the radiation decomposition of water can be represented by these reactions:

TABLE I

## RADIATION YIELDS OF SUCCINIC ACID AND HYDROGEN PEROXIDE

Radiation, 35 Mev Helium Ions; Beam Intensity, 0.20 Microamperes;  
Dose,  $3.8 \times 10^{20}$  ev/ml

Acetic Acid Conc <u>M</u>	A-Evacuated Solutions (Cell 3)		B-Mechanically Stirred, Helium Aerated (Cell 2)	
	$G_s$	$G_{H_2O_2}$	$G_s$	$G_{H_2O_2}$
0.0625	0.17	0.29	0.14	0.23
0.125	0.26	0.33	0.23	0.26
.25	0.28	0.35	0.31	0.28
.50	0.30	0.37	0.35	0.31
1.00	0.32	0.40	0.36	0.34

G-molecules of product/100 ev



where reaction 2 represents the combination of the radicals in region of high ionization density and 1 represents the formation of radicals which are available for reactions with decomposition products or with added solute. Reaction 2 is favored

over reaction 1 as the ionization density of the effective radiation increases. The production of succinic acid is most readily accounted for by assuming that the  $\text{CH}_2\text{COOH}$  radical<sup>10</sup> is formed as an intermediate. Presumably this proceeds principally via



rather than



since it has been found in the irradiation of  $\text{CD}_3\text{COOH}$  solution that HD accounts for less than seven per cent of the evolved product hydrogen. Succinic acid is formed by the reaction,



If we consider a competition in which OH radicals produced in 1 react either with product (P) resulting from 2 or with acetic acid (M) and if we employ the usual procedures in deriving a rate law from a mechanism we obtain the following relationship:

$$k_1 I = k_p (P)(\text{OH}) + k_3 (M)(\text{OH}) \quad (6)$$

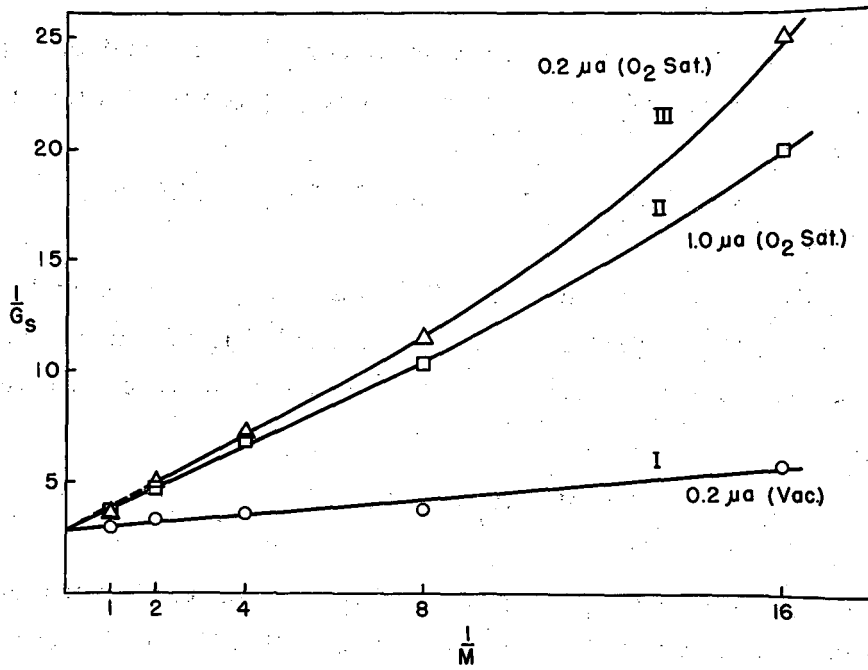
where  $k_1$  is the yield of reaction 1,  $k_p$  the rate constant for the reaction of OH with P,  $k_3$  the rate constant for the reaction of M with OH and I the radiation intensity. For low radiation doses the equation for the formation of succinic acid becomes

$$\frac{d(S)}{dt} = \frac{k_1}{2} (M) (\text{OH})$$

substituting in 6 and taking P as a constant we obtain<sup>8</sup>

$$\frac{I}{G_s} = \frac{2}{k_1} \left[ 1 + \frac{C}{(M)} \right] \quad (7)$$

where  $G_s$  is the experimentally observed radiation yield of succinic acid and C is a constant involving P. A plot of  $1/G_s$  against  $1/(M)$  for the yield data obtained in evacuated systems at a beam intensity of 0.20 microamperes (Table 1A) is shown in curve I Fig. 11. A straight line is obtained which if extrapolated to  $1/(M) = 0$  gives  $k_1 \approx 0.80$ .



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Fig. 11. Effect of acetic acid concentration (M) on the yield of succinic acid in evacuated and oxygen aerated solutions.

The results of similar concentration studies in oxygen aerated solution at 0.20 microamperes and 1.0 microamperes are represented in Fig. 11 by curves III and II respectively. The effect of oxygen is to decrease the yield of succinic acid at the lower concentrations. The fact that, with the same conditions of aeration, the 1.0 microampere data show higher G values for succinic acid production indicates that an even greater oxygen effect could be observed if sufficient oxygen could be introduced into the irradiation zone. The results of a series of helium ion irradiations in which the solutions were mechanically stirred and at the same time aerated with a stream of oxygen are shown in Table II. It is seen that at high stirring rates, the succinic acid yield is decreased to zero. Since mechanical stirring in evacuated solutions has no appreciable effect on the yield, it is concluded that the data of Table II represent a true oxygen effect. That a decrease in the succinic acid yields

TABLE II

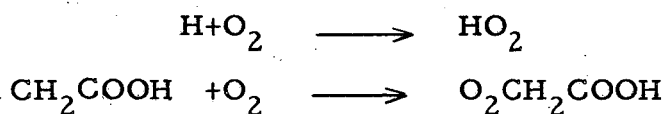
EFFECT OF STIRRING ON RADIATION YIELDS OF SUCCINIC  
ACID AND HYDROGEN PEROXIDE IN 0.25 M ACETIC ACID  
SOLUTION AERATED WITH OXYGEN

Radiation, 35 Mev Helium Ions; Beam Intensity, 0.20 Microamperes;  
Dose,  $3.8 \times 10^{20}$  ev/ml

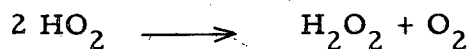
Stirring Speed (r. p. m.)	$G_s$	$G_{H_2O_2}$
None	0.14	0.48
300	0.078	0.73
600	0.060	0.80
1200	0.031	0.94
1700	0.00	1.01

and an increase in the hydrogen peroxide yields are not the only experimentally observed effects of oxygen aeration is shown in Table III. These data, obtained with sealed targets, show a pronounced increase in the radiation yield of

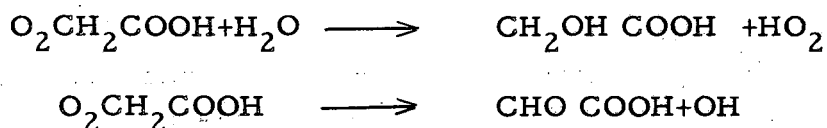
carbon dioxide in solutions containing oxygen. These results suggest that both H and  $\text{CH}_2\text{COOH}$  react with oxygen



hydrogen peroxide is then formed by



The  $\text{O}_2\text{CH}_2\text{COOH}$  radical may react to form glycolic acid or glyoxylic acid by reactions of the type<sup>11, 12</sup>



These acids could then be oxidized preferentially via oxalic acid to give carbon dioxide. A detailed discussion of the effect of oxygen on the radiolysis of acetic acid will appear in a forthcoming publication.

To determine the effect of ionization density on radiation yields in evacuated acetic acid solutions, a series of irradiations has been made with 18 Mev deuterons at a dose rate and total dose identical with that used in the helium ion studies shown in Table I. These data are compared in Table IV. The radiation yield of the products shown, with the exception of carbon dioxide and methane, increase with acetic acid concentrations and level off in the region 1 to 2 M. Since the range of a deuteron of energy E is twice that of a helium ion of energy 2E, the average ionization densities along the tracks are in the ratio 1/4. The relatively greater radical yield in deuteron irradiated systems should result in a higher yield of succinic acid and a lower yield of hydrogen peroxide as compared to the helium ion case. A comparison of the hydrogen yields in Table IV is of interest in view of Hart's recent work<sup>13</sup> on the formic acid-oxygen system in which the radiation yield for water decomposition via reactions 1 and 2 is a constant

TABLE III

EFFECT OF OXYGEN ON RADIATION YIELDS IN  
0.25 M ACETIC ACID SOLUTION

Radiation, 35 Mev Helium Ions; Beam Intensity, 0.20 Microamperes;  
Dose,  $3.8 \times 10^{20}$  ev/ml

Product	Radiation Yield (G)	
	Evacuated	Oxygen Present
Succinic Acid	0.28	0.14
Hydrogen Peroxide	0.35	0.70
Hydrogen	0.96	0.75
Carbon Dioxide	0.10	0.49

TABLE IV

EFFECT OF IONIZATION DENSITY ON RADIATION  
YIELDS IN 1 M ACETIC ACID SOLUTION

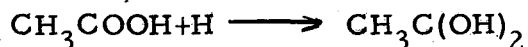
Beam Intensity, 0.20 Microamperes; Dose  $3.8 \times 10^{20}$  ev/ml

Radiation Yield (G)

Product	Deuterons (18 Mev)	Helium Ions (35 Mev)
Succinic Acid	0.59	0.32
Hydrogen Peroxide	0.24	0.39
Hydrogen	1.52	1.00
Carbon Dioxide	0.39	0.28
Methane	0.11	0.08



equal to approximately 3.4 and is independent of ionization density. Since the reaction of H with acetic acid contributes less than seven per cent of the total product hydrogen, the observed hydrogen yield should approach 1.7 at the higher acetic acid concentration if it is assumed that all of the H recombine. This is apparently the situation for the deuteron case as shown in Table IV. With the more densely ionizing helium ions, however, the hydrogen yield reaches a limiting value which is not above 1.0. One possible explanation for the lower hydrogen value observed in the helium ion irradiation is that the mechanical agitation given the sealed target cells is not sufficient to remove reaction products from the irradiation zone as the ionization density of the radiation increases. That this is not the case is shown by the results previously shown in Table III. If, however, the competing reactions occur within the track volume stirring would, of course, have no effect. Another possibility is that the H radical reacts at the higher acetic concentration via a competing reaction of the type



These processes will be considered in detail in forthcoming publications.

### ACKNOWLEDGEMENTS

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